



Low cost biosorbent “banana peel” for the removal of phenolic compounds from olive mill wastewater: Kinetic and equilibrium studies

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ABSTRACT

The aim of this work is to determine the potential of application of banana peel as a biosorbent for removing phenolic compounds from olive mill wastewaters. The effect of adsorbent dosage, pH and contact time were investigated. The results showed that the increase in the banana peel dosage from 10 to 30 g/L significantly increased the phenolic compounds adsorption rates from 60 to 88%. Increase in the pH to above neutrality resulted in the increase in the phenolic compounds adsorption capacity. The adsorption process was fast, and it reached equilibrium in 3-h contact time. The Freundlich and Langmuir adsorption models were used for mathematical description of the adsorption equilibrium and it was found that experimental data fitted very well to both Freundlich and Langmuir models. Batch adsorption models, based on the assumption of the pseudo-first-order, pseudo-second-order and intraparticle diffusion mechanism, showed that kinetic data follow closely the pseudo-second-order than the pseudo-first-order and intraparticle diffusion. Desorption studies showed that low pH value was efficient for desorption of phenolic compounds. These results indicate clearly the efficiency of banana peel as a low-cost solution for olive mill wastewaters treatment and give some preliminary elements for the comprehension of the interactions between banana peel as a bioadsorbent and the very polluting compounds from the olive oil industry.

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1. Introduction

Olive mill wastewaters (OMW) are a significant source of environmental pollution related to olive oil production industries. Olive oil extraction processes generate three phases: olive oil, solid residue and aqueous liquor (OMW) which averagely represents 20, 30 and 50%, respectively, of the total weight of the processed olives. OMW cause serious environmental deteriorations such as coloring of natural waters, alteration of soil quality, phytotoxicity and odor nuisance.

Since olive oil is mainly produced in the Mediterranean region (95% of the world production), countries from this area are particularly concerned by this environmental problem. About 11 million tons of olives are produced each year in this region from which about 1.7 million tons of olive oil is extracted. The seasonal polluting load of olive oil production is reported to be equivalent to that of 22 million people per year [1].

Conventional methods for the removal of phenolic compounds from OMW can be divided into three main categories: biological

[2–4], chemical [5–7] and physical treatment [1,8,9]. Among them, physical adsorption method is generally considered to be the best, effective, low cost and most frequently used method for the removal of phenolic compounds. Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications. Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [10]. Adsorption also does not result in the formation of harmful substances and the organic sorbents can be used as fuel for power generation or as ferment substrate.

The most popular and widely used adsorbent material for treatment of OMW is activated carbon [11,12]. However, the relatively high initial cost and the need for a costly regeneration system make the activated carbon less economically viable as excellent adsorbent [13,14].

Many sorbents based on low cost agricultural by-products had been used for dye sorption from wastewater, which included banana pith [15], orange peel [16], wheat straw [17], sawdust [18], powdered waste sludge [19], wheat shells [20], wheat bran [21] and hen feathers [22]. However, at the best of our knowledge, the adsorption and removal of specific organics from OMW by banana peel has not been reported.

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The purpose of this work is to investigate the efficiency of banana peel as a biosorbent for removal of phenolic compounds from OMW. Banana peel is an abundant and low cost agricultural waste residue and is easily available in large quantities. The effects of various operating parameters on biosorption such as initial pH, sorbent dosage and contact time were monitored and optimal experimental conditions were determined. Different adsorption isotherms (Langmuir and Freundlich isotherms) and kinetic models (pseudo-first, pseudo-second-order kinetics and intraparticle diffusion) were used to find out most suitable models describing our experimental findings.

2. Experimental

2.1. OMW origin

OMW were obtained from a three-phase continuous extraction unit from Marrakech, southern Morocco. The OMW were first stored in a plastic can (120 L-capacity) at ambient (20–30 °C) temperature.

2.2. Preparation of the adsorbent

Banana peel was from a local market. The collected biomaterial was extensively washed under tap water to remove any particulate, sprayed with distilled water. This biosorbent was cut into small pieces, dried in sunlight, crushed and sieved through a 1 mm size before its use in adsorption experiments without any further treatment.

2.3. Physical–chemical analysis of OMW

pH was determined with a pH meter (716 DMS Titrimo). Electrical conductivity (EC) was measured with a conductivimeter (Tacussel) [23]. Total solids (TSs) were obtained by weighing sample before and after drying overnight at 105 °C. Total suspended solid (TSS) was determined after filtering a sample through a GF/C filter (0.45 μm) and drying the retained residue at 105 °C for 60 min. Mineral matter was determined after calcination at 450 °C for 4 h. The difference between TS and mineral matter was defined as volatile solids (VSs) [23].

Total and dissolved chemical oxygen demand (COD) was determined by a colorimetric method [24]. An appropriate amount of sample was introduced into a commercially available digestion solution and the mixture was then incubated for 120 min at 150 °C in a COD reactor. COD concentration was measured colorimetrically using UV/VIS spectrophotometer (500 serie DU). The absorbance was determined at 620 nm.

The biochemical oxygen demand (BOD₅) was assessed by measuring the oxygen uptake in a sample over a period of 5 days at 20 °C, in the dark, using the BOD Track apparatus. The sample was diluted, mixed with domestic wastewater and its pH was adjusted. As dissolved oxygen was consumed, air pressure in the bottle dropped and pressure changes were continuously recorded [25].

Kjeldahl N (Kj-N) was determined by the Kjeldahl digestion and distillation method. Ammoniacal nitrogen (NH₄) was determined colorimetrically according to AFNOR method [25]. Nitrite (NO₂) was determined by coupling diazotation followed by a colorimetric method according to AFNOR method [25]. Nitrate (NO₃) was determined like nitrite after its reduction by passage in a cadmium–copper column [23].

The phosphorus content (expressed as phosphate equivalents) was determined colorimetrically using the AFNOR method [25].

Chloride (Cl⁻) was determined by a titrimetry method according to AFNOR method [25].

Reducing sugars were determined by a colorimetric method according to Dubois et al. [26].

Table 1

Chemical and physical properties of banana peel used in the experiments.

Parameters	Data
Moisture content (%)	13.55
Volatile matter (%)	86.44
Ash (%)	3.85
C content (%)	31.79
O content (%)	42.87
K content (%)	14.86
Na content (%)	1.33
Si content (%)	1.48
Al content (%)	1.05
Cl content (%)	3.22
pH	6.60
Particle size (mm)	<1

Density was determined by weighing an exactly measured volume of sample.

Phenolic compounds were quantified by means of the Folin–Ciocalteu colorimetric method [27] using caffeic acid as a standard. The absorbance was determined at 765 nm. Chromatographic separations of phenolic substances were carried out on C-18 column (5 mm, 4.6 mm × 250 mm) using H₃PO₄ (0.1%)–water–acetonitrile/water (7/3) mobile phase system. The HPLC system consisted of an injector with a 20-μL sampling loop and a UV–visible spectrophotometric detector. Detection was performed at 280 nm and an isocratic elution rate was 0.8 mL/min.

K⁺, Na⁺ and Ca²⁺ were analysed with a flame photometry method.

2.4. Physical–chemical analysis of adsorbent

Surface images of the adsorbent before and after adsorption were captured by scanning electron microscopy (SEM), with a JEOL JSM-5500 apparatus. Rates of volatile matter, ash and moisture were determined by Rodier method [23]. Results summarized in Table 1 show the measured characteristics. Chemical analysis of the banana peel showed that major constituents are carbon, potassium and oxygen, Na, Si, Al and Cl has been found in traces.

2.5. Adsorption experiments

Batch adsorption experiments were carried out using a rotary shaker (rotatest 74581) at 200 rpm min⁻¹ at 30 ± 2 °C in a 250-mL shaking flasks containing 100 mL of OMW with a known concentration of phenol (13.45 g/L). Different doses (1–5 g) were tested at various pHs (2–11). pH studies were conducted to determine the optimum pH at which maximum phenolic compounds removal could be achieved. The pH of the suspension was adjusted by 0.1N HCl or NaOH. The flasks were sealed to prevent change in volume of the solution during the experiments. The changes of adsorption rates of phenols were monitored at different time intervals (1; 1.5; 2; 2.5; 3; 4; 18; 24 h). Samples were taken out from flasks and the solutions were separated from the adsorbent by filtration with a 0.6-mesh stainless steel sieve and centrifuged for 20 min at 5100 rpm min⁻¹. Phenolic compounds concentration in the supernatant solutions was determined. The experiments conducted in duplicate and the negative controls (without adsorbent) were simultaneously carried out.

The amount of adsorption at equilibrium, q_e (mg/g) and the percent adsorption (%) was computed as follows:

$$q_e = \frac{(C_0 - C_{eq})V}{X} \quad (1)$$

$$\text{percent adsorption (\%)} = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

where C_0 and C_{eq} are the initial and equilibrium concentration of phenolic compounds (g/L), V volume of solution (L), X the weight of banana peel (g) and C the phenolic concentration at the end of adsorption.

2.6. Desorption experiments

The adsorbent (3 g) used for the adsorption experiments of OMW at pH 7 was separated from the solution by centrifugation and washed gently with water to remove any unadsorbed phenolic compounds. Desorption experiments were conducted on 1 g of used adsorbent which was agitated at 200 rpm min^{-1} for 12 h with 100 mL of: neutral pH water, water at pH 12 and water–acetic acid (pH 1.20).

3. Results and discussion

3.1. OMW characterization

Table 2 shows the main properties of OMW after 1-week decantation to remove the total suspended solids. As depicted in Table 2, the sample shows an acidic pH value (5.06). Due to this relatively low pH value, biological treatment of OMW may be limited by the ability of micro-organisms to grow at such acidic pH. In general, bacteria show maximum growth at pH between 6.5 and 7.5 [28]. If the pH of OMW is not modified prior to discharge, they may alter the pH of natural waters [29]. The electrical conductivity was very low (6.9 mS/cm) compared to that reported by Zenjari et al. which varies between 25.3 and 36.6 mS/cm [30]. This parameter may be directly related to salting practices of the olives before trituration according to some Moroccan traditional practices.

OMW show high concentrations of total solids (20.4 g/L) and total suspended solids (2.07 g/L). The high TS of the raw OMW make it unsuitable for irrigation use. Number of farms in rural areas in Morocco, occasionally, uses raw OMW for irrigation aiming benefits of its high fertilizing value.

OMW contain also a high level of organic matter (70.2 g O_2 /L of total COD, 48.7 g O_2 /L of dissolved COD) and high amounts of total phenolic compounds (13.4 g/L) which are known highly phytotoxic. The content of phenolic compounds in OMW is usually higher than the standard limits (mostly less than 0.5 mg/L) established for their release into aquatic environment.

Table 2

Physical–chemical determination of the raw OMW (mean values of three separate analysis \pm standard deviation).

Parameters	Data
pH (25 °C)	5.06
Electrical conductivity (mS/cm) at 20 °C	6.85
Total suspended solid (TSS) (g/L)	2.07 ± 0.02
Total solid (TS) (g/L)	20.41 ± 0.4
Mineral matter (MM) (g/L)	5.29 ± 0.05
Volatile solid (VS) (g/L)	1.51 ± 0.03
TKN (g/L)	1.96 ± 0.01
NH_4^+ (mg/L)	0.64 ± 0.04
NO_3^- (mg/L)	0.40 ± 0.07
NO_2^- (mg/L)	4.00 ± 0.03
Total phenols (g/L)	13.45 ± 0.01
Total COD (g O_2 /L)	70.22 ± 1.22
Dissolved COD (g O_2 /L)	48.69 ± 3.18
BOD_5 (g O_2 /L)	16.74 ± 0.19
PO_4^- (g/L)	0.36 ± 1.43
Total P (g/L)	0.42 ± 0.003
Cl^- (g/L)	1.42 ± 0.001
K^+ (g/L)	2.11 ± 0.00
Ca^{2+} (g/L)	0.06 ± 0.00
Na^+ (g/L)	0.46 ± 0.00
Reducing sugar (g/L)	0.12 ± 0.008
Density (g/L)	1.10 ± 0.02

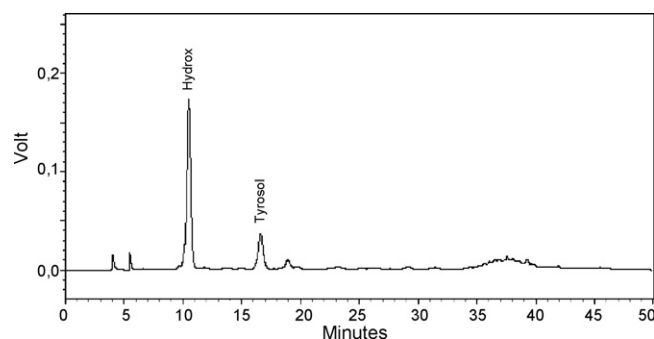


Fig. 1. HPLC chromatograms of the phenolic compounds from raw olive mill effluent.

Total COD were higher than those reported by some Moroccan researchers [31,32]. Total phenolic compounds concentrations were also higher than those obtained by other authors [32–34]. These differences in the levels of phenolic compounds may be due to the variety and the degree of maturity of the processed olives [35] and also to the extraction techniques used. Caponio and Catalano have shown that even the temperature of the olives before and during crushing influences strongly the solubilization of phenolic compounds and consequently their amounts in OMW [36].

HPLC chromatograms depicted in Fig. 1 show Hydroxytyrosol (0.275 g/L) and tyrosol (0.062 g/L) as the two main monomer phenolic compounds encountered in our samples. Such composition is almost similar to that reported by other researchers [37]. As determined by the HPLC analysis the phenolic compounds content is found to be less than that obtained by the Folin-Ciocalteu determination. The Folin-Ciocalteu method is known to be not specific to phenolic compounds, other molecules can react with this reagent leading to an over estimation of the phenolic content.

The OMW contain some valuable nutrients such as nitrogen and potassium, which would be useful in agriculture after effluent treatment. The high concentrations of sodium (0.46 g/L) and chloride (1.4 g/L) were probably due to salting of the olives.

3.2. Preliminary adsorption tests

Preliminary tests were carried out at two concentrations of adsorbents (1% and 5%) at ambient temperature, under agitation and 1-day contact time. The results (Table 3) showed that with 1% of banana peel, we obtained an elimination of 34%, 11.5% and 16% of phenolic compounds, COD and color intensity, respectively. The increase of this amount of adsorbent to 5% improved the elimination of the phenolic compounds (66%), COD (54%) and color intensity (67%) (Table 3).

The HPLC analysis of the residual phenolic compounds of the OMW after adsorption on the banana peel at a concentration of 1% (Fig. 2a) shows an elimination of 41% of the hydroxytyrosol and 34% of the tyrosol. With 5% of the bioadsorbent, the treatment allowed an important elimination of monomeric compounds, 90% of hydroxytyrosol and 56% of tyrosol (Fig. 2b).

3.3. SEM analysis

SEM has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. It is

Table 3

Efficiency of reducing pollutant charges in OMW using banana peels as bioadsorbent.

Banana peel (%)	% polyphenols	% COD	% coloration
1	34	11.5	16
5	66	54	67

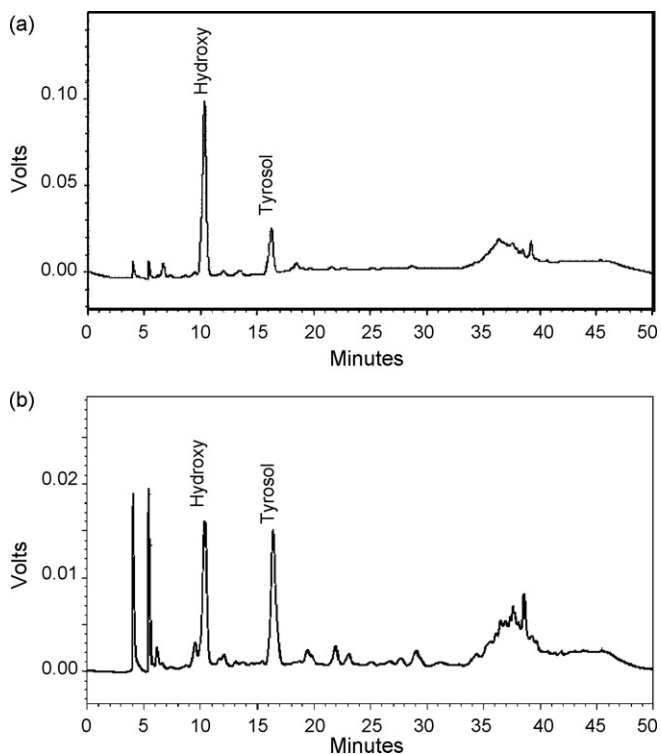


Fig. 2. (a) HPLC analysis of the phenols from OMW after treatment with 1% of banana peel and (b) HPLC analysis of the phenols from OMW after treatment with 5% of banana peel.

useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent.

The chemical characterization of the powder before and after adsorption showed a change of the characteristics of the surface of the powder (Table 4). The difference in percentage of each element before and after adsorption demonstrates the change of the characteristics of the surface of the banana peel powder, and confirms the adsorption phenomenon.

Scanning electron micrographs of original banana peel (Fig. 3a) show that the peel particles pores are highly heterogeneous. After adsorption, a significant change in the structure of the peel is observed (Fig. 3b). The peel appears to have a rough surface with crater-like pores because they are partially covered by organic molecules.

3.4. Effect of adsorbent rates

Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The equilibrium uptake for the adsorption of phenolic compounds on banana peel was determined with 100 mL of OMW containing 13.45 g/L total phenolic compounds. The system was agitated for 24 h (200 rpm) at a constant temperature ($30 \pm 2^\circ\text{C}$) at the initial pH 5. Fig. 4 shows that the increase in adsorbent dosage from 10 to 50 g/L resulted in a decrease from 13.45 to 0.34 g/L in of phenolic compounds of the OMW. It is readily understood that the number of available adsorption sites increases with

Table 4
Chemical characterization of the powder before and after adsorption.

	Elements						
	C	O	K	Na	Si	Al	Cl
% before adsorption	31.8	42.8	14.8	1.33	1.48	1.05	3.22
% after adsorption	40.11	47.7	2.37	5.02	0.74	0.70	1.03

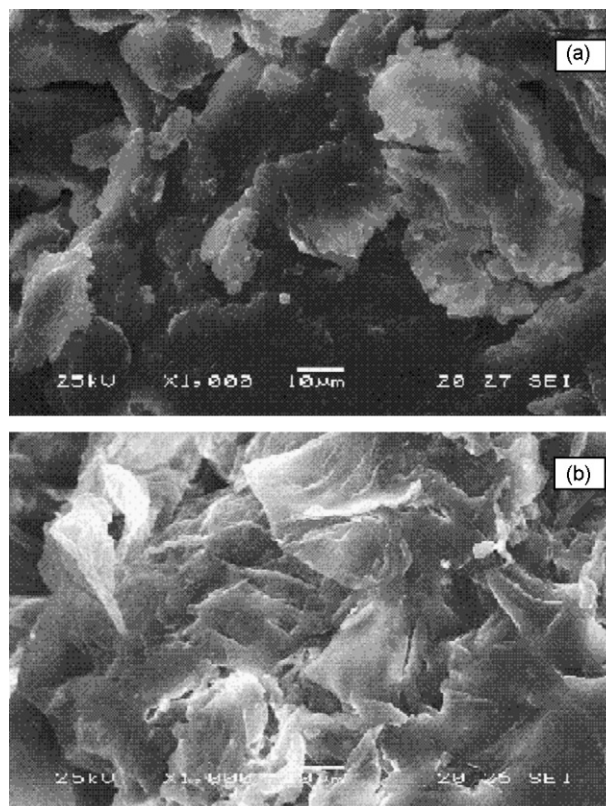


Fig. 3. (a) SEM images for original banana peel and (b) SEM images for banana peel after adsorption.

the increase in the adsorbent dosage and it, therefore, results in the increase in the amount of adsorbed phenolic compound. The increase in adsorbent rate over 30 g/L has not allowed any additional improvement in adsorption. This seems to be due to the binding of almost molecules of phenolic compounds to the sorbent and the establishment of equilibrium between the molecules bounded to the sorbent and unadsorbed molecules in the solution. Thus, all our subsequent experiments were performed at an adsorbent dosage of 30 g/L.

The adsorption capacity was found to be high at low dosages. Many factors can contribute to this adsorbent concentration effect. The most important factor is that adsorption sites remain unsaturated during the adsorption reaction. This decrease in adsorption capacity with the increase in the adsorbent dosage is mainly attributed to the non-saturation of the adsorption sites during the adsorption process [38,39].

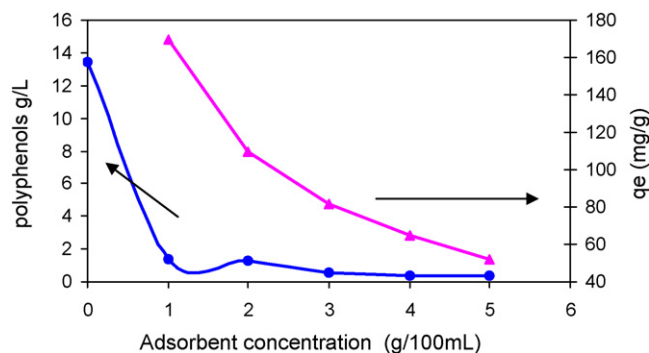


Fig. 4. Influence of adsorbent concentration on adsorption rates of phenolic compounds and the equilibrium uptake (conditions: 100 mL of OMW, temperature: 30°C , contact time: 24 h and initial pH 5).

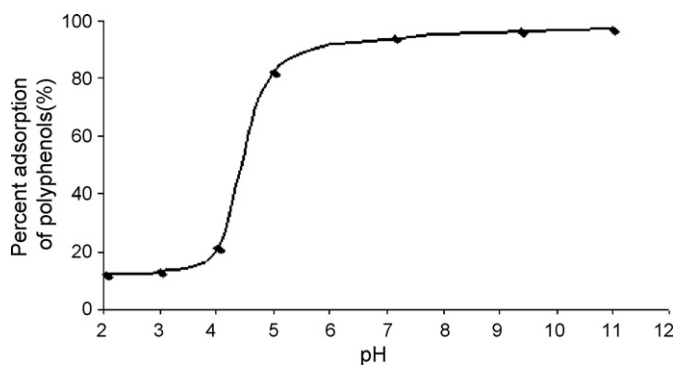


Fig. 5. Effect of pH on adsorption of phenolic compounds by banana peel (conditions: 100 mL of OMW, temperature: 30 °C, contact time: 24 h and sorbent dose: 30 g/L).

3.5. Effect of pH on phenolic compounds biosorption

The most important parameter influencing the adsorption capacity is the pH of adsorption medium [40]. The final pH of an adsorption medium affects the adsorption mechanisms on the adsorbent surface and influences the nature of the physico-chemical interactions of the species in solution and the adsorptive sites of adsorbents [41]. The experiments of the pH effect were conducted on 100 mL OMW. Agitation was maintained for 24 h (200 rpm) at (30 ± 2 °C) at the predetermined optimal adsorbent dosage (30 g/L).

The effect of pH on the adsorption of phenolic compounds by banana peel at pH ranging between 2 and 11 is shown in Fig. 5. The adsorption efficiency increased from 12% (10.45 g/L) to 90% (0.3 g/L) when the solution pH varied from 2 to 7. Little improvement was obtained above neutrality. As it is well established, pH affects the degree of ionization of the phenolic compounds. Banana peel material is composed of various functional groups, such as amino and carboxyl, which could also be affected by the pH.

When $\text{pH} = \text{pKa}$, the anion and neutral forms will be 50% respectively. With the increase of the pH, the anion form increases while neutral form decreases. The neutral form can be neglected when $\text{pH} > \text{pKa}$ more than 2 units. At higher pH values the concentration of the negatively charged phenoxide ion increases. At lower pH values, phenolic compounds are present as the acidic compounds [42].

As shown in Fig. 5, at low pH values, the rate of the sorbed phenolic compounds was very low. At higher pH, the adsorption increased and stabilized from pH 7 to 11. Thus high elimination (96%) of natural phenolic compounds in OMW is achieved in a large pH zone above neutrality. From a practical point of view, this will be of great interest, since it will not necessitate very accurate adjustment of the medium pH.

Controversially, Thawornchaisit and Pakulanon [43], Aksu and Yener [10] studying adsorption of phenols on dried sludge, reported an increase of adsorption at lower pH values, and a decrease at higher pH values. Many other authors who have obtained similar behavior stated an adsorbent surface charge modification. As the pH of the system increases, the number of negatively charged sites increases which must be less favorable to the adsorption of phenolate ions due to electrostatic repulsion [44,45].

However, in other studies we can find appreciable adsorption rates at alkaline pH. Works of Lin et al. demonstrated that an increase of the pH to high-alkalinity (pH 8–11) resulted in an increase in the phenol adsorption capacity on hydroxyapatite nanopowders [46]. Namasivayam et al. reported significant removal of anionic dyes using banana pith as bioadsorbent at alkaline pH [47]. Similar behavior was obtained with sawdust used for treat-

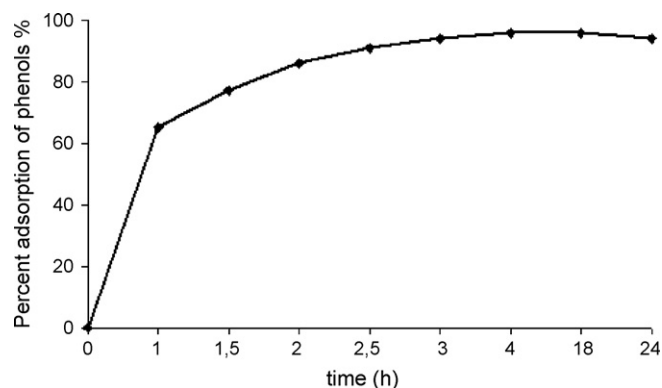


Fig. 6. Effect of contact time on adsorption of phenolic compounds by banana peel (conditions: 100 mL of OMW, temperature: 30 °C, sorbent dose: 30 g/L and pH 7).

ment of textile industry effluents [18]. In this latter study almost 100% dye removal was obtained at pH values above 7.

The mechanisms of action of pH cannot be reduced to a surface charge modification and the adsorption of phenolic compounds and other compounds must not be seen only as the result of electric interactions. Many other interactions can lead to adsorption of molecules on adsorbent surfaces especially in the case of bioadsorbents. Adsorption can result from weak forces interactions, ionic strength and chemical reactions leading to irreversible bindings. However, the mechanisms involved governing the effect of pH on phenolic compounds adsorption mechanism need to be further investigated.

3.6. Effect of contact time

Effect of contact time on adsorption of phenolic compounds by banana peel is presented in Fig. 6. The adsorption equilibrium of phenolic compounds was obtained after 3 h with an adsorption of approximately 96% of the phenolic compounds. Almost, no remarkable improvement was observed after longer contact time. Adsorption rate of phenolic compounds on banana peel was found to be relatively much faster than those reported for some other normal adsorbents. Xiaolo and Youcai investigated the adsorption of phenolic pollutants in the aqueous solution by aged-refuse [48] and reported that the remaining concentration of the phenolic pollutants in the liquid phase becomes asymptotic to the time axis after 4 h of shaking. Thawornchaisit and Pakulanon determined that the sorption equilibrium of phenol on dried sewage sludge was reached within 20 h [49]. Adsorption of bromophenols onto carbonaceous adsorbents derived from fertilizer solid waste was performed by Bhatnagar [50] and reported an equilibrium time of about 8 h.

Initially, large number of vacant surface sites is available for adsorption; the adsorption rate is very fast thus increases rapidly the amount of adsorbates accumulated on the banana peel surface mainly within the first hour of adsorption. As a result, the remaining vacant surface sites are difficult to be occupied due to formation of repulsive forces between the phenolic compounds on the solid surface and the bulk phase [51]. The phenolic compounds have to penetrate deeper into the pores encountering much higher resistance [52]. This can explain the decrease of adsorption rates which is well illustrated by the plateau line after 3 h adsorption.

The HPLC analysis of the residual phenolic compounds of the OMW after adsorption on the banana peel at a concentration of 30 g/L, pH 7 and at 3 h shows an elimination of 94% of the hydroxytyrosol and 100% of the tyrosol.

Nevertheless, it must be notice that the residual concentration of the phenolic substances remain above of the limit authorized by

legislation (0.5 mg/L). As the OMW contains in addition to the phenolic substances many other types of compounds such as sugars, aminoacids, and proteins a competition may occur for adsorption on specific sites. This may contribute to lower removal efficiency of the phenolic substances. Further elimination of these latter substances is needed before discharging these wastewaters in nature. Such a complete removal may be achieved by a system with series of adsorption units.

Subsequent sorption steps may probably lead to a complete elimination of these pollutants.

3.7. Adsorption isotherms

Adsorption is the accumulation of a mass transfer process that can generally be defined as material at the interface between solid and liquid phases. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium.

In order to optimize the design of a sorption system to remove phenolic compounds from OMW, it is important to establish the most appropriate correlation for the equilibrium curve. Many theories which describe adsorption equilibrium were applied. Several isotherm equations are available, and two important isotherms are selected for this study: the Langmuir and Freundlich [53,54]. The linearised Langmuir equation is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \quad (3)$$

where q_e (mg/g) and C_e (g/L) are the amount of adsorbed phenolic compounds per unit weight of adsorbent and the unadsorbed phenolic compounds concentration in solution at equilibrium. b is the equilibrium constant or Langmuir constant related to the affinity of binding sites (L/g) and Q_m represents a particle limiting adsorption capacity when the surface is fully covered with phenolic compounds and assists in the comparison of adsorption performance.

This equation has been successfully applied to many adsorption processes [7–14]. The Langmuir isotherm was developed on the assumption that the adsorption process will only take place at specific homogenous sites within the adsorbent surface with uniform distribution of energy level. Once the adsorbate is attached on the site, no further adsorption can take place at that site; which concluded that the adsorption process is monolayer in nature. The essential characteristic of the Langmuir isotherm can be expressed by the dimensionless constant called the equilibrium parameter, R_L , defined as:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where b is the Langmuir constant, C_0 is the initial phenolic compounds concentration (g/L) and R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$) [55]. Our results show that the adsorption for phenolic compounds on the banana peel is favorable and has an R_L value between 0 and 1 (Table 5).

Table 5
Isotherm constants and the correlation coefficients of Langmuir and Freundlich isotherms.

Effluent	Langmuir isotherm				Freundlich isotherm		
	Q_m (mg/g)	b (L/g)	R_L^2	R_L	K_F	n	R_F^2
OMW	688.9	0.24	0.94	0.57	0.13	1.13	0.99

Also, data were studied with the Freundlich isotherm, which can be expressed by logarithmic form as

$$\ln q_e = \ln K_F + \frac{1}{n \ln C_e} \quad (5)$$

where K_F is a Freundlich constant that shows adsorption capacity of adsorbent, n is a constant which shows greatness of relationship between adsorbate and adsorbent. Freundlich isotherm was based on the assumption that the adsorption occurs on heterogeneous sites with non-uniform distribution of energy level. The Freundlich describes reversible adsorption and is not restricted to the formation of monolayer. It has been found that the adsorption for phenolic compounds on the banana peel is favorable and has an n value between 1 and 10 (Table 5).

The equilibrium isotherm for the adsorption of phenolic compounds on banana peel was determined with 100 mL of OMW with a known concentration of phenolic compounds (13.45 g/L). The system was agitated for 24 h (200 rpm) in a constant temperature (30 °C) at initial pH 5. Fig. 4 shows the adsorption isotherms of phenolic compounds (q_e versus C_e) using banana peel. The Q_m , b , R_L , R_L^2 (correlation coefficient for Langmuir isotherm), K_F , n , and R_F^2 (correlation coefficient for Freundlich isotherm) are given in Table 5.

The R_L^2 and R_F^2 values shown in Table 5 are evidence that the phenolic compounds adsorption in this study is well fitted to both Langmuir and Freundlich models; a possibility of mono and heterolayer phenolic compounds formation on the adsorbent surface. This observation is not rare as similar findings have been reported before [56–58]. This phenomenon can be further explained by understanding the surface chemistry of banana peel. The presence of active functional groups with different intensity and non-uniform distribution may cause differences in the energy level of the active sites available on the banana peel surface thus affecting its adsorption power. Active sites with higher energy level tend to form heterolayer phenolic compounds coverage with robust support from strong chemical bonding while active sites with lower energy level will induce monolayer coverage due to electrostatic forces.

From the comparison of the adsorption capacity of different type of low-cost adsorbent used for removal of phenols and phenolic compounds (Table 6), the banana peel showed a high adsorption capacity of phenolic compounds (688.9 mg/g).

3.8. Kinetics of the adsorption process

3.8.1. Kinetic model of phenolic compounds adsorption

Adsorption kinetics has been proposed to elucidate the adsorption mechanism. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbent as well as on the mass transport process. In order to investigate the mechanism of phenolic compounds adsorption on the banana peel and examine the potential rate-controlling step, i.e., mass transfer or chemical reaction. The capability of pseudo-first-order and pseudo-second-order kinetic models was examined in this study.

The pseudo-first-order equation [62,63] is

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (6)$$

where q_e and q_t refer to the amount of phenolic compounds adsorbed (mg/g) at equilibrium and at any time, t (h), respectively, k_1 (h^{-1}) is the equilibrium rate constant of pseudo-first-order sorption.

On the other hand, a pseudo-second-order equation [62,63] based on the adsorption capacity is expressed in the form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

where k_2 is the rate constant for pseudo-second-order kinetics (g/g h).

Table 6
Langmuir and Freundlich constants for phenol and phenolic compounds adsorption by various adsorbents reported in literature.

Adsorbent	Adsorbate	Q_m (mg/g)	b (L/g)	K_F	n	References
Activated coal	Phenol	1.84	0.065	0.79	0.79	[57]
Resin AP-246		0.071	0.584	0.112	0.35	
Resin OC-1074		0.043	0.445	0.0053	0.16	[59]
Carbonised beet pulp	Phenol	◇	◇	29.35	5.13	[46]
Hydroxyapatite	Phenol	◇	◇	0.37	1.66	[56]
Coconut shell	Phenol	205.84	3.91	37.11	3.66	[48]
Aged-refuse	Phenol	◇	◇	0.019	1.19	
	2-Chlorophenol	◇	◇	0.042	1.22	
	4-Chlorophenol	◇	◇	0.195	1.59	
	2,4-Dichlorophenol	◇	◇	0.180	1.50	
Palm pith carbon	2,4-Dichlorophenol	19.16	0.70	*	*	[60]
Paper mill sludge	2,4-Dichlorophenol	4.49	0.003	*	*	[61]
Banana peel	Phenolic compounds	688.9	0.24	0.13	1.13	This study

◇ Does not follow Langmuir isotherm/not reported. * Does not follow Freundlich isotherm/not reported.

Table 7
Kinetics constants and the correlation coefficients for different kinetic models.

Effluent	Pseudo-first-order				Pseudo-second-order		
	$q_{(e,exp)}$ (mg/g)	$q_{(e,cal)}$ (mg/g)	k_1 (h^{-1})	R_1^2	$q_{(e,cal)}$ (mg/g)	k_2 (g/g h)	R_2^2
OMW	688.9	200.03	0.88	0.82	370.3	12.82	0.99

The pseudo-first-order and pseudo-second-order equation, k_1 , k_2 , correlation coefficients, theoretical and experimental q_e values were compared in Table 7.

As shown in Table 7, the correlation coefficient of pseudo-second-order equation is higher than that of pseudo-first-order and the theoretical q_e value calculated from pseudo-second-order was more close to the experimental q_e value than from pseudo-first-order. It can be concluded that the pseudo-second-order kinetic model fits for the adsorption of phenolic compounds on the banana peel. It indicates chemical sorption in the adsorption process, which may be partly due to the hydrogen-binding between the hydroxyl groups of phenolic compounds and the active functional groups in the banana peel, and it may be the rate-limiting step.

3.8.2. Diffusion model

Since neither the pseudo-first-order and pseudo-second-order kinetic model can identify the diffusion mechanism, the intraparticle diffusion model [64] was also used to analyze and elucidate the diffusion mechanism. The intraparticle model is expressed as

$$q_t = k_p t^{1/2} + C \quad (8)$$

where q_t is the amount of phenolic compounds adsorbed at equilibrium (mg/g) at time t , C is the intercept and k_p is the intraparticle diffusion rate constant ($g/g h^{1/2}$).

In order to quantify the applicability of the model, the correlation coefficient was calculated from the plot as in Table 8. It is clear to see that the R_2^2 value for pseudo-second-order kinetic model is much higher than these for the intraparticle diffusion kinetic model and the coefficient is lower than that of the pseudo-second-order model. Therefore, this section suggested that the pseudo-second-order model is the best choice among the three kinetic models to describe the adsorption behavior of phenolic compounds onto banana peel, suggesting that the pseudo-second-order adsorption

Table 8
The parameter of the intraparticle diffusion model.

Effluent	OMW
k_p ($g/g h^{1/2}$)	0.021
C (g/g)	0.28
R_3^2	0.42

mechanism is predominant and the overall rate of the adsorption process appears to be controlled by the chemical reaction.

3.9. Desorption studies

Desorption studies can further aid in elucidating the mechanism of adsorption. The studies of Namasivayam and Yamuna showed that if the adsorbed dye on the solid surface can be desorbed by water, demonstrating that the attachment of the dye on the adsorbent is by weak bonds. If alkaline water (pH 12) is needed, then the adsorption is by ion exchange. If organic acids, like acetic acid, are the most efficient for desorption, then the adsorption is held by the adsorbent through chemisorption [65,66].

Neutral pH water (pH 7.3), acetic acid (pH 1.2) and alkaline water (pH 12) have shown 0.17, 0.30 and 0.12 g/g of desorbed amounts of phenolic compounds, respectively. This indicates that various mechanisms contribute to the adsorption of phenolic compounds on banana peel but chemisorption might be the main mechanism.

The adsorption of phenolic compounds increased in an alkaline medium and decrease in an acidic medium. As the pH of the system decreases, the number of positive charged sites increased. A positively charged surface site on the adsorbent favours the desorption of phenolic compounds due to electrostatic repulsion. At pH 1.2, a significantly high electrostatic repulsion exists between the positively charged surface of the adsorbent and phenolic compounds.

4. Conclusion

Banana peel has proven to be a promising material for the removal of contaminants from olive mill wastewaters. Not only banana peel is an abundant cheap adsorbent, but also it is highly efficient for removing phenolic compounds from OMW. All those add more credits to banana peel for removing pollutants from wastewaters. The main characteristics of the adsorption process of the natural phenolics from OMW on banana peel can be summarized as follows:

- The banana peel showed a high adsorption capacity of phenolic compounds (689 mg/g), revealing that banana peel could be

employed as a promising adsorbent for phenolic compounds adsorption.

- The adsorption process was very fast, and it reached equilibrium in 3 h of contact. The equilibrium solid-phase concentration of phenols (q_e , w/w) decreased with increasing adsorbent (banana peel) concentration is mainly attributed to the unsaturation of the adsorption sites through the adsorption process. The equilibrium was reached at 82.33 mg/g (3 g/100 mL) of banana peel.
- The pH played an obvious effect on the phenolic compounds adsorption capacity onto banana peel. An increase of the solutions pH leads to a significant increase in the adsorption capacities of phenolic compounds on the banana peel, maximum adsorption capacity occurred at alkaline pH.
- Both Langmuir and Freundlich isotherms provide good correlations for the adsorption of phenolic compounds onto banana peel.
- The pseudo-second-order kinetic model was found to represent the experimental data better than pseudo-first-order model and intraparticle diffusion with a better fit ($R_2^2 > 0.99$).
- Desorption experiments showed an almost chemisorption interactions between the natural phenolic and the adsorption sites on the banana peel.

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